o-Nitroaniline Derivatives. Part 12.[1] The Reaction of *N*-(2,4-Dinitrophenyl)-sarcosine Ethyl Ester with Bases: Some Novel Redox Processes Revealed by *X*-Ray Crystallography

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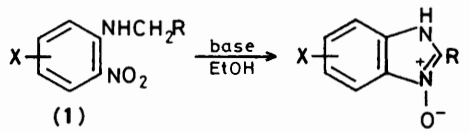
According to the base used, the title reaction gives either 2-amino-2′-methylamino-5,5′-dinitro-*ONN*-azoxybenzene (**9**) or 2,2′-bis(methylamino)-5,5′-dinitroazoxybenzene (**10**), together with 1-hydroxy-4-methyl-7-nitroquinoxaline-2,3-dione (**13**). Reaction of compound (**13**) with thionyl chloride gives 5-chloro-1-methyl-6-nitroquinoxaline-2,3-dione (**12**). Possible mechanisms for these novel reactions are discussed.

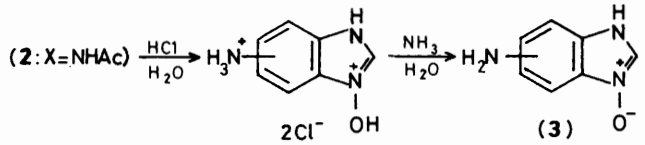
The structures of (*i*) the diacetyl derivative [*viz.* (**8**)] of the azoxy compound (**9**), (*ii*) compound (**12**), and (*iii*) the monohydrate of (**13**), have been established by *X*-ray crystallography. All three compounds give monoclinic crystals. Compound (**8**) has space group $P2_1/n$, with 4 molecules in a cell of dimensions $a = 19.949(4)$, $b = 10.289(4)$, $c = 9.101(2)$ Å, $\beta = 97.98(2)°$; $R = 0.030$ for 1 270 reflections. Compound (**12**) has space group $P2_1/c$, with 4 molecules in a cell of dimensions $a = 6.922(1)$, $b = 10.857(3)$, $c = 13.192(2)$ Å, $\beta = 100.87(1)°$; $R = 0.055$ for 956 reflections. Compound (**13**)·H_2O has space group $C2/c$, with 8 formula units in a cell of dimensions $a = 16.130(3)$, $b = 7.173(1)$, $c = 18.215(3)$ Å, $\beta = 97.67(2)°$; $R = 0.037$ for 1 244 reflections.

In the last three parts of this series,[1-3] we have described a general method whereby *N*-(*o*-nitroaryl)glycine derivatives (nitriles or esters) (**1**) are cyclised in basic media to benzimidazole *N*-oxides (**2**), and we have shown how the method



(**1**) (**2**)

(R = CN or CO_2Et)

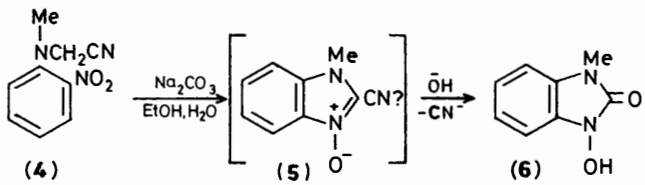


Scheme 1.

may be adapted to the synthesis of aminobenzimidazole *N*-oxides of the type (**3**) (Scheme 1). We have now turned our attention to the synthesis of selectively alkylated analogues of (**3**), and in this connection we have examined the reactions of *N*(*o*-nitroaryl)sarcosine derivatives with bases.

Livingstone and Tennant have shown[4] that the nitrile (**4**) corresponding to *N*-(*o*-nitrophenyl)sarcosine undergoes cyclisation in base to give 1-hydroxy-3-methylbenzimidazolone (**6**) rather than the expected nitrile (**5**), although the latter may be formulated as an intermediate (Scheme 2). Our investigation has therefore centred on *N*-(*o*-nitroaryl)sarcosine esters.

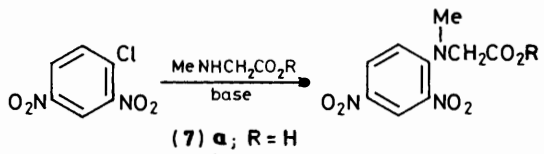
The most accessible of these esters are those derived from *N*-(2,4-dinitrophenyl)sarcosine (**7a**), since they may be obtained by nucleophilic displacement reactions of 1-chloro-



(**4**) (**5**) (**6**)

Scheme 2.

2,4-dinitrobenzene. Surprisingly, the ethyl ester (**7b**) is prepared as easily, and in higher yield, *via* the acid (**7a**) than by direct reaction of the chlorodinitrobenzene with ethyl sarcosinate. Although the latter reaction, in the presence of triethylamine,



(**7**) **a**; R = H
b; R = Et

does give some of the required (bright yellow) ester, the product is contaminated by a bright red by-product, $C_{14}H_{14}N_6O_5$ (referred to below as compound **A**). Compound **A** is also obtainable by renewed treatment of the ester (**7b**) with triethylamine in ethanol.

Reaction of the ester (**7b**) with sodium ethoxide (1 mol equiv.) in ethanol–dimethylformamide at room temperature gives a red–brown precipitate which is separable into two main components by extraction with boiling acetone. The acetone extract, on evaporation, gives a second red compound, **B** ($C_{13}H_{12}N_6O_5$), and the acetone-insoluble portion is a sodium salt which, on dissolution in water followed by acidification (HCl), gives a buff-coloured acidic compound, **C** ($C_9H_7N_3O_5$). Compounds **B** and **C** are also obtained, although in different proportions, by the reaction of (**7b**) with potassium carbonate,

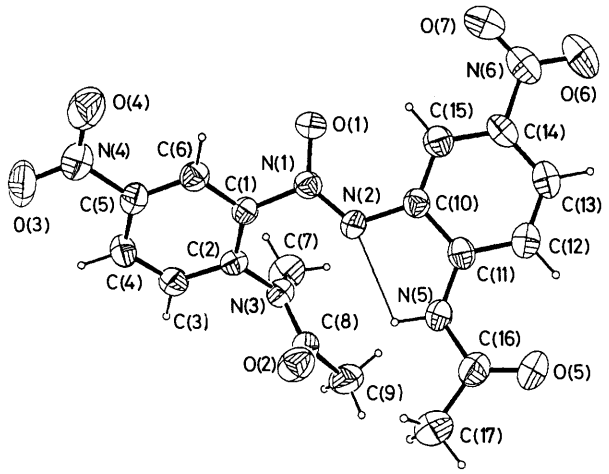


Figure 1. A view of molecule (**8**). Ellipsoids are at the 50% level. Hydrogen atoms are shown as small spheres of an arbitrary size.

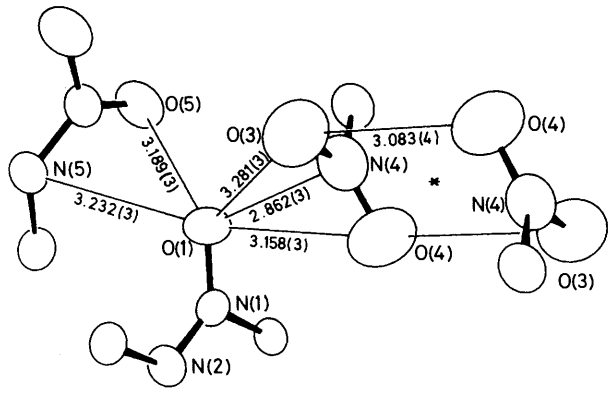


Figure 2. Details of the environment about the azoxy group in (**8**). See also Table 6(*c*).

and a trace (*ca.* 1%) of **C** is formed, along with **A**, in the reaction of (**7b**) with triethylamine.

Structures of Compounds **A** *and* **B**.—There is no doubt from the high-field (360 MHz) ^{1}H n.m.r. spectra of **A** and **B** (Table 1) that they are close structural relatives; they differ only in that **A** contains two (non-equivalent) methylamino groups, and **B** contains one methylamino and one primary amino group.

Both compounds crystallise in the form of fine fibrous needles, and as such are not amenable to *X*-ray crystallographic analysis. The *N*,*N*′-diacetyl derivative of **B**, however, can be so studied, and has the structure (**8**) shown in Figure 1. It follows that **B** has the structure (**9**), and by analogy **A** is assigned the structure (**10**).

Structure of Compound **C**.—The acidic product **C** is not 1-methyl-5-nitrobenzimidazole-2-carboxylic acid 3-oxide (**11**), as we had originally supposed from its spectroscopic properties. Its reaction with thionyl chloride gives a chloro compound, $C_9N_6ClN_3O_4$, which has been shown by *X*-ray crystallography to have the quinoxalinedione structure (**12**) (Figure 3); this implies the structure (**13**) for compound **C** itself. Structure (**13**) has been confirmed by *X*-ray crystallography: although the anhydrous form of **C** (fine needles from acetic acid) cannot be studied in this way, we have obtained an efflorescent hydrate from dimethylformamide–ethanol which has the structure shown in Figure 4.

X-*Ray Crystallographic Analysis.*—*Compound* (**8**) (*Figure 1*). The most remarkable feature of this structure is the intra-

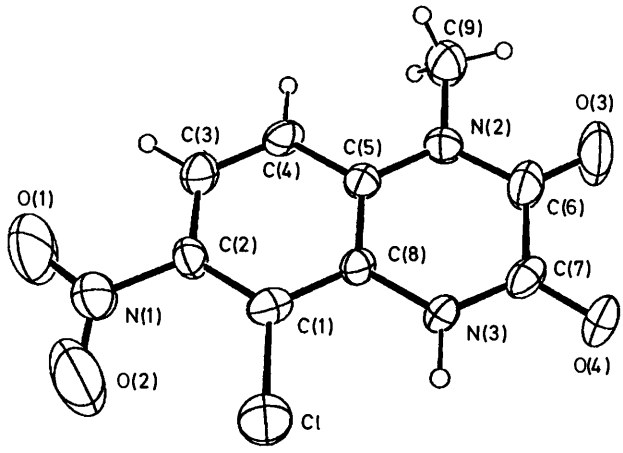


Figure 3. A view of molecule (**12**).

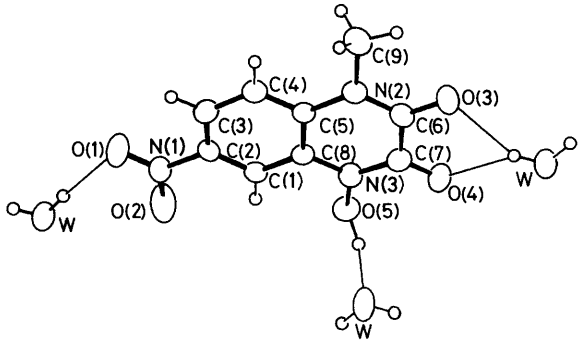
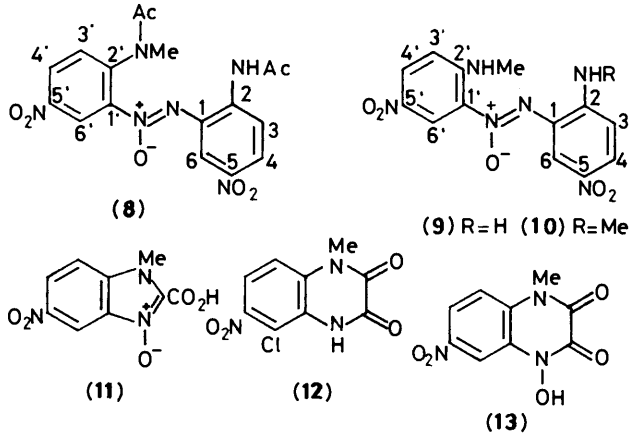


Figure 4. A view of molecule (**13**) showing the hydrogen bonding scheme involving the water molecule; details are in Table 8(*c*).



molecular hydrogen bond between the amino hydrogen of the acetamido group and the adjacent azoxy nitrogen [N · · · N 2.622(3) Å]. This interaction serves not only to bring these *ortho*-located nitrogens closer together [the angles N(2)–C(10)–C(11) and C(10)–C(11)–N(5) being 112.3° and 118.8°, respectively]; it is also conformation-determining for a substantial part of the molecule, since it effectively locks the atoms of the azoxy and acetamido groups into the same approximate plane as the benzene ring C(10)–C(15). This results, in turn, in the amide carbonyl group being in close proximity to the *ortho*-hydrogen on the ring, a feature which accounts, presumably, for the large chemical-shift difference between this proton (3-H in Table 1) and its counterpart (3′-H) in the other ring [$\Delta\delta$ = 1.24: *cf.* $\Delta\delta$ = 0.09 for the corresponding protons in compound (**9**)]. There is no analogous conformational restriction in the other benzene ring: there the bulky *N*-methylacetamido substituent

Table 1. ^{1}H and ^{13}C N.m.r. spectra of azoxybenzene derivatives.

^{1}H spectra

	Chemical shifts (δ)								Coupling constants/Hz				
Compound	3-H	3′-H	4-H	4′-H	6-H	6′-H	*N*-substituents	*N*′-substituents	3,4	3′,4′	4,6	4′,6′	Other
(**9**)[a]	6.97d	6.88d	8.20dd	8.04dd	8.74d	9.40d	7.16s (NH_2)	2.97d (CH_3) 8.12q (NH)	9.4	9.25	2.7	2.65	CH_3, NH 4.9
(**10**)[a]	6.99d	6.83d	8.24dd	8.16dd	8.72d	9.39d	2.92d (CH_3) 7.32q (NH)	2.97d (CH_3) 8.04q (NH)	9.4	9.4	2.7	2.7	CH_3, NH (both rings) 5.0
(**8**)[b]	7.59d	8.83d	8.49dd	8.31dd	8.69d	9.30d	2.29s ($COCH_3$) 8.77s (NH)	1.61s ($COCH_3$) 3.42s (NCH_3)	8.7	9.3	2.4	2.4	—

The assignments are confirmed, where necessary, by decoupling

^{13}C spectra (provisional assignments)

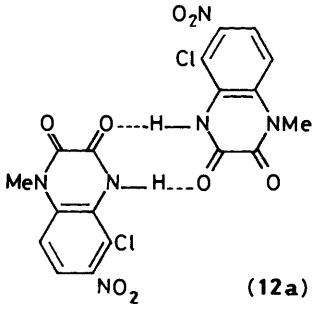
Compound	C-1	C-1′	C-2	C-2′	C-3	C-3′	C-4	C-4′	C-5	C-5′	C-6	C-6′	NCH_3	$N'CH_3$
(**9**)[a]	125.8	131.1	152.0	147.7	114.4	112.4	126.8	127.5	134.5	134.6	122.0	119.2	—	29.9
(**10**)[a]	126.5	131.3	150.8	147.7	109.6	112.3	127.3	127.5	134.1	134.6	122.1	118.4	29.7	29.9

[a] 360 MHz for ^{1}H; 90.56 MHz for ^{13}C. [b] 300 MHz for ^{1}H; $CDCl_3$ solution.

is accommodated by rotation of this ring by 35° relative to the rest of the molecule, and alignment of the substituent atoms approximately at right angles to the plane of the ring.

The dimensions of the azoxy group [N=N, 1.278(3); N–O, 1.256(3) Å] are consistent with its formulation as shown in (**8**). The intermolecular contacts around the oxygen [O(1)] are entirely consistent with its carrying a formal negative charge. Oxygen O(1) makes a number of such close contacts (Figure 2), the shortest being to the nitro nitrogen N(4) of an adjacent molecule with O • • • N 2.862(3) Å. There are no intermolecular hydrogen bonds in the crystal structure.

Compound (**12**) (*Figure 3*). This exists in the crystal as a centrosymmetric dimer (**12a**), with the two individual molecules



(**12a**)

linked by a pair of N–H • • • O hydrogen bonds [N • • • O, 2.949(5) Å]; the carbon–oxygen bond lengths [1.202(6) and 1.211(5) Å] leave no doubt that the molecule is correctly represented as the dione tautomer. The steric interaction between the adjacent chloro and nitro substituents is accommodated by the plane of the latter being rotated by 13° from that of the ring system.

Compound (**13**)·H_2O (*Figure 4*). Although molecules of this type have also been formulated[5,6] as 3-hydroxyquinoxalin-2-one 4-oxides, the carbon–oxygen [1.220(3) and 1.210(3) Å] and nitrogen–oxygen [N(3)–O(5) 1.386(2) Å] bond lengths, together with the location of the hydroxy hydrogen, establish the *N*-hydroxyquinoxalinedione structure in the crystal. In the absence of the neighbouring chloro substituent, the nitro group and the ring system are effectively co-planar, and the single water molecule engages in hydrogen bonding in three ways as shown in Figure 4 and detailed in Table 8(*c*). One hydrogen interacts with a nitro oxygen [O(1)] and the other forms a bifurcated hydrogen bond with the two carbonyl oxygens; whereas the water oxygen interacts with the (acidic) hydroxy hydrogen.

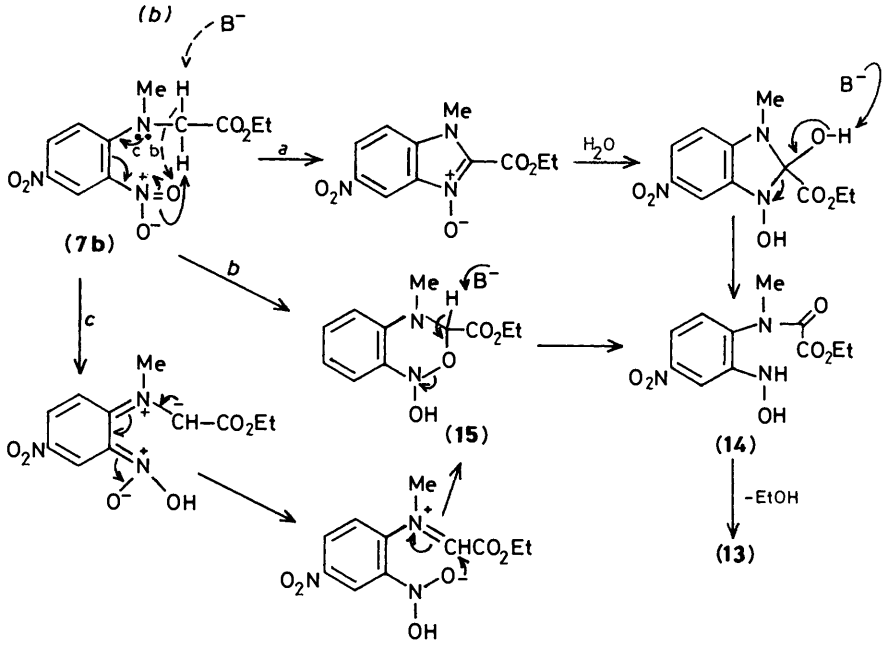
Mechanism.—The formation of the azoxybenzene derivatives (**9**) and (**10**), and the *N*-hydroxyquinoxalinedione (**13**), from the ester (**7b**) each present an interesting mechanistic problem, as does the further conversion of (**13**) into (**12**) by reaction with thionyl chloride.

Formation of the N-*hydroxyquinoxalinedione* (**13**). This is the easiest of the three processes to rationalise mechanistically, since the structural relationship of the product to the starting compound is reasonably obvious. The quinoxaline is most probably formed by cyclisation of the *o*-hydroxylamino ester (**14**),[7] which in turn may result from an intramolecular redox reaction of the (isomeric) starting ester (**7b**). We have commented elsewhere[8] on the synthetic utility of this reaction.

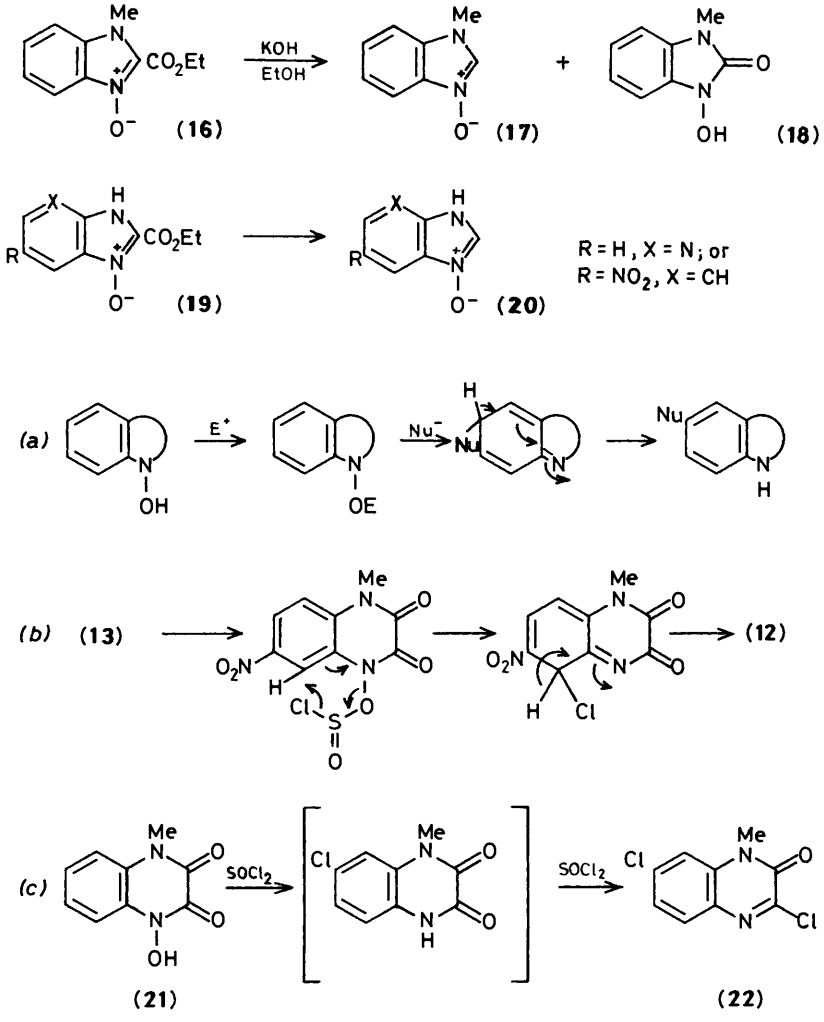
Several possible mechanisms are shown in Scheme 3. The first (pathway *a*) involves the 'normal' cyclisation to a benzimidazole *N*-oxide (*cf.* Scheme 1), followed by addition of water and base-induced ring-opening. A second (pathway *b*) involves intramolecular nucleophilic attack at the oxygen of the nitro-group, and ring-opening of the resulting oxadiazine intermediate (**15**). This intermediate (**15**) may also be generated in other ways, as for example in pathway *c*.

Whether the redox reaction (**7b**)→(**14**) is intramolecular, as required by pathways *b* and *c*, or whether the amide oxygen of (**14**) has its origin in an external reagent, as required by pathway *a*, is still a matter of speculation, although labelling experiments designed to distinguish between these are now receiving our attention. Although there is excellent analogy for the first step of pathway *a* (*cf.* Scheme 1), the remaining steps are without literature precedent: indeed Takahashi and Kano have shown[9] that reaction of the related *N*-oxide (**16**) with ethanolic alkali gives a mixture of (**17**) and (**18**), involving *total loss* of the ester function, and we ourselves have observed similar processes, *viz.* (**19**)→(**20**), under relatively mild basic conditions.[10] At present, therefore, we tend to favour a reaction pathway which involves the oxadiazine (**15**), especially since an alternative base-induced ring-opening of the latter provides a possible route to the azoxy-compounds (**9**) and (**10**) (see below).

Reaction of the N-*hydroxyquinoxalinedione* (**13**) *with thionyl chloride.* Electrophilic attack at the oxygen atom of an *N*-hydroxy heterocycle (or an *N*-oxide) is often followed by an S_N' reaction [Scheme 4(*a*)].[11] In the case of the reaction (**13**)→(**12**),

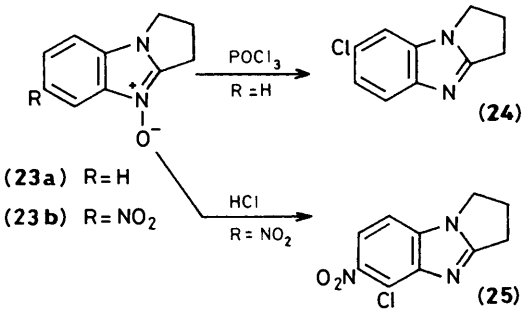


Scheme 3.



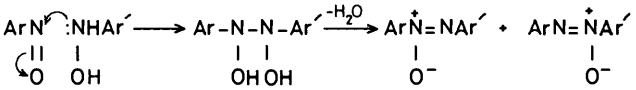
Scheme 4.

the (apparently exclusive) introduction of chlorine at the 5-position, *i.e. ortho* to the nitrogen bearing the leaving group, suggests the possibility of an intramolecular mechanism involving a six-membered transition state [Scheme 4(*b*)]. However, the corresponding reaction of the un-nitrated analogue (**21**)[5] leads to introduction of the chlorine at the 7-(*para*) position, a process which cannot be intramolecular [Scheme 4(*c*)].* The same type of regioselectivity in S_N' reactions has also been reported in the case of some fused benzimidazoles, *viz.* (**23a**)→(**24**) and (**23b**)→(**25**),[12] and in that series an intramolecular mechanism seems unlikely.



Formation of the azoxy compounds (**9**) *and* (**10**). Azoxybenzene derivatives are commonly obtained by reduction of nitro- or nitroso-benzenes in basic media, and alcoholic solutions of strong bases (hydroxides or alkoxides) are often sufficient to bring about such reduction (the alcohol being oxidised to aldehyde or carboxylic acid).[13] In these reactions, however, other substituents in the nitro- or nitroso-benzene are generally retained intact in the final product, whereas in the formation of (**9**) and (**10**) there is no immediately obvious mechanism whereby the CH_2CO_2Et groups may be lost under these basic conditions.

The formation of compound (**9**) is also extraordinary in that one (and specifically one) of the *N*-methyl groups is lost in the course of the reaction. Unsymmetrically substituted azoxybenzenes are known to result from the interaction of a nitrosobenzene and an *N*-arylhydroxylamine (Scheme 5), but



Scheme 5.

mixtures of isomers generally result, and in the present case there is no indication (by n.m.r. spectroscopy) that an isomer of (**9**) is produced.

In considering possible mechanisms for the conversion (**7b**)→(**9**) or (**10**), it is obviously important to determine the fate of the CH_2CO_2Et moiety of (**7b**), and also of the *N*-methyl carbon in the case of (**9**). The following results are relevant in this context.

(*i*) *N*-Methyl-2,4-dinitroaniline[14] does not react with bases under the same conditions as the ester (**7b**): loss of the CH_2CO_2Et moiety from (**7b**) by a simple nucleophilic displacement may therefore be discounted.

(*ii*) Reaction of the ester (**7b**) with triethylamine in the presence of *o*-phenylenediamine (1 mol equiv.) gives a low yield (16%) of quinoxalin-2-one (**16**);[15] the yield of the azoxy compound (**10**) is also substantially higher than in the absence of the diamine (48% instead of 16%). The formation of (**16**) implies that the CH_2CO_2Et fragment is lost, in part at least, as ethyl glyoxylate, $OHCCO_2Et$.

(*iii*) The reaction of the ester (**7b**) with sodium ethoxide produces formaldehyde, which was detected in small amounts by distilling the volatile components of the reaction mixture into 2,4-dinitrophenylhydrazine solution. The detected yield must be considered minimal, since a control experiment showed that an authentic sample of formaldehyde could not be recovered in high yield from this solvent mixture by distillation.

We believe that the mechanism outlined in Scheme 6 is in accord with all the above observations. The two key intermediates are the oxadiazine (**15**), which is also a proposed intermediate in the conversion (**7b**)→(**13**), and *N*-methyl-4-nitro-2-nitrosoaniline (**26**),† which may be formed from (**15**) by tautomeric ring-opening followed by loss of ethyl glyoxylate. Reduction of the nitrosoaniline in the basic media (ethyl glyoxylate, indeed, being one possible reducing agent) may then give the symmetrically substituted azoxybenzene (**10**).

We formulate the conversion of the nitrosoaniline (**26**) into the unsymmetrically substituted azoxybenzene (**9**) as follows. In the presence of bases stronger than triethylamine, (**26**) may be partially isomerised into the *o*-hydroxlaminoanil (**27a**) or its cyclic tautomer (**27b**), and reaction with unchanged nitrosoaniline then leads to the oxadiazine (**28**). Elimination of formaldehyde from the latter would then give the required azoxybenzene derivative (**9**).

We are continuing to explore the mechanistic details and the synthetic potential of these reactions, and we shall report further in due course.

Experimental

I.r. spectra were recorded for Nujol mulls. ^1H N.m.r. spectra were recorded at 80 MHz, and ^{13}C n.m.r. spectra at 75.5 MHz, in $(CD_3)_2SO$ unless otherwise indicated. U.v.–vis. spectra were recorded in $CHCl_3$.

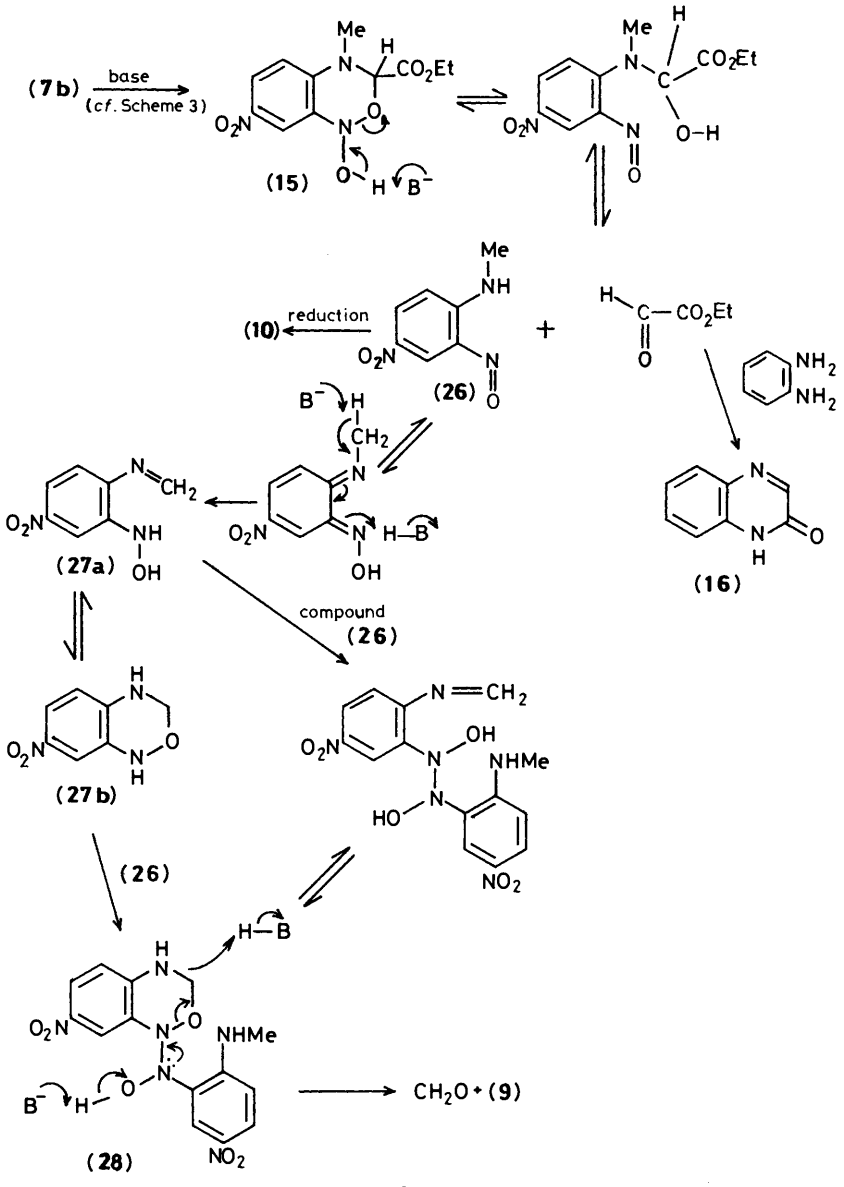
N-(2,4-*Dinitrophenyl*)*sarcosine* (**7a**).—A solution of sarcosine (14.63 g, 0.16 mol) and sodium hydrogen carbonate (41 g, 0.48 mol) in water (250 cm^3) was added to a stirred solution of 1-chloro-2,4-dinitrobenzene (30.0 g, 0.15 mol) in ethanol (500 cm^3) at room temperature. The mixture was heated under reflux for 6 h, concentrated under reduced pressure to *ca.* 200 cm^3, and extracted with ether; acidification (HCl) of the aqueous layer gave compound (**7a**) (36.2 g, 96%), m.p. 170–172 °C (lit.,[18] 176 °C, lit.,[19] 185–186 °C), which was esterified directly without further purification.

N-(2,4-*Dinitrophenyl*)*sarcosine Ethyl Ester* (**7b**).—(*i*) A solution of the acid (**7a**) (25 g) in ethanol (300 cm^3) containing dry hydrogen chloride (7.5 g) was heated under reflux for 5 h, then cooled, and the yellow–green *ester* filtered off and recrystallised twice from ethanol (with charcoal). Yield, 22.4 g (81%), m.p. 103 °C. (Found: C, 46.4; H, 4.6; N, 14.8. $C_{11}H_{13}N_3O_6$ requires C, 46.65; H, 4.6; N, 14.8%). $\nu_{max.}$ 1 740 (CO), 1 520 and 1 330 cm^{-1} (NO_2); δ_H 1.24 (3 H, t, CH_3CH_2), 2.97 (3 H, s, CH_3N), 4.20 (2 H, q, CH_2CH_3), 4.38 (2 H, s, CH_2N), 7.24 (1 H, d, 6-H), 8.26 (1 H, dd, 5-H), 8.61 (1 H, d, 3-H); $J_{CH_3CH_2}$ 7 Hz, $J_{3,5}$ 3 Hz, $J_{5,6}$ 9.5 Hz.

(*ii*) Ethyl sarcosinate hydrochloride (7.6 g, 0.05 mol) was added at room temperature to a stirred mixture of 1-chloro-2,4-dinitrobenzene (10.0 g, 0.049 mol), triethylamine (10.0 g, 0.099 mol), and ethanol (250 cm^3). The mixture was heated under reflux for 5 h, then cooled to *ca.* 40 °C, filtered, and the red solid

* Dr. G. Tennant (University of Edinburgh) has informed us that members of his research group have, independently, obtained similar results. Their detailed findings will be published elsewhere.

† *N*-Methyl-4-nitro-2-nitrosoaniline has previously been isolated in small quantities from the photolysis of *N*-(2,4-dinitrophenyl)-*N*-methylleucine[16] or *N*-(2,4-dinitrophenyl)sarcosine.[17]



Scheme 6.

washed with ethanol. 2,2′-*Bis*(*methylamino*)-5,5′-*dinitroazoxybenzene* (**10**) (0.50 g, 6%) had m.p. 276–277 °C (from dimethylformamide) (Found: C, 48.45; H, 4.1; N, 24.3. $C_{14}H_{14}N_6O_5$ requires C, 48.6; H, 4.1; N, 24.3%). $\nu_{max.}$ 3 410 and 3 225(NH), 1 530w and 1 325 cm^{-1} (NO_2); $\lambda_{max.}$ 283, 373, and 456 nm (log ε 4.12, 4.25, and 3.83); n.m.r. spectra, see Table 1; *m/z* 346 ($M^{+\cdot}$, 64%), 330 (9), 329 (9), 167 (30), 166 (100), 165 (23), 164 (59), 135 (34), 120 (23), 119 (18), 118 (68), 105 (50), *etc.* The reaction mother liquor was concentrated to *ca.* 200 cm^3, and cooled to room temperature; the precipitate was filtered off, redissolved in the minimum volume of boiling ethanol, and the solution filtered while hot, then treated with charcoal, and cooled to give the *ester* (**7b**) (4.08 g, 29%), m.p. 97–100 °C, identical spectroscopically with the product from (*i*).

When triethylamine (3 mol equiv.) was used, the azoxybenzene (**10**) was recovered in 14% yield.

Reactions of the Ester (**7b**) *with Bases.*—(*i*) *With sodium ethoxide.* A solution of the ester (**7b**) (2.0 g, 7.1 mmol) in dimethylformamide (30 cm^3) was added dropwise, with stirring, to a solution of sodium ethoxide (from sodium, 0.16 g, 1 mol equiv.) in ethanol (50 cm^3) at room temperature. Stirring was continued for 3 h, and the solid product was then filtered off and extracted exhaustively with boiling acetone. The red extract gave on evaporation 2-*amino*-2′-*methylamino*-5,5′-*dinitro*-ONN-*azoxybenzene* (**9**) (0.38 g, 32%), m.p. 259 °C (from acetic acid) (Found: C, 46.8; H, 3.6; N, 25.3. $C_{13}H_{12}N_6O_5$ requires C, 47.0; H, 3.6; N, 25.3%); $\nu_{max.}$ 3 460 and 3 330 (NH and NH_2), 1 535w and 1 330 cm^{-1} (NO_2); $\lambda_{max.}$ 315sh, 366, and 438 nm (log ε 4.16, 4.53, and 4.23); n.m.r. spectra, see Table 1; *m/z* 332 ($M^{+\cdot}$, 41%), 316 (9), 315 (9), 314 (15), 300 (12), 269 (12), 182 (12), 181 (9), 165 (15), 164 (76), 163 (12), 153 (41), 152 (100), 137 (12), 121 (18), 118 (88), 105 (76), *etc.*

The acetone-insoluble, buff-coloured product was dissolved in water; acidification (HCl) gave 1-*hydroxy*-4-*methyl*-7-*nitroquinoxaline*-2,3-*dione* (**13**) (0.32 g, 19%), m.p. 243 °C (decomp.) (from acetic acid) (Found: C, 45.3; H, 2.9; N, 17.6. $C_9H_7N_3O_5$ requires C, 45.6; H, 3.0; N, 17.7%). $\nu_{max.}$ 1 660br (CO), 1 515, and 1 325 cm^{-1} (NO_2); δ_H 3.58 (3 H, s, CH_3), 7.63 (1 H, d, 5-H), 8.11 (1 H, dd, 6-H), 8.19 (1 H, d, 8-H), and 11.5–12.5 (1 H, br s, OH); $J_{5,6}$ 9 Hz, $J_{6,8}$ 3 Hz; δ_C 30.6 (CH_3), 107.8 (C-8), 115.8 (C-5), 119.2 (C-6), 127.9 (C-8a), 130.8 (C-4a), 142.7 (C-7), 150.1 (C-3), and 155.2 (C-2); *m/z* 237 ($M^{+\cdot}$, 43%), 221 (100), 109 (47), 193 (27),

Table 2. Data collection and refinement details.

Compound	(8)	(12)	(13)·H_2O
Crystal size/mm	0.20 × 0.30 × 0.30	0.20 × 0.25 × 0.25	0.15 × 0.17 × 0.25
2θ Range/°	2–45	2–54	2–54
ω-Scan width	0.60 + 0.35 tan θ	0.70 + 0.35 tan θ	0.60 + 0.35 tan θ
Reflections measured	3 120	2 414	2 631
Unique reflections	2 606	2 121	2 268
Averaging R factor	0.015	0.018	0.019
Reflection with $I > 3\sigma(I)$	1 270	956	1 244
R	0.030	0.055	0.037
R_w	0.041	0.078	0.051
p in $w = 1/(\sigma^2Fo + pFo^2)$	0.040	0.050	0.050
Extinction correction, g	7×10^{-7}	—	7×10^{-7}
Max. shift/error in final cycle	<0.005	0.01	0.01
Goodness of fit	1.71	2.39	1.49
No. of variables in final cycle	272	154	164
Final delta-map peaks (e $Å^{-3}$)	0.16	0.44	0.21

Table 3. Compound (**8**): positional parameters and their estimated standard deviations.

Atom	x	y	z
O(1)	0.028 99(9)	0.225 6(2)	0.587 1(2)
O(2)	−0.209 0(1)	0.373 4(2)	0.395 3(2)
O(3)	−0.068 8(1)	−0.134 0(3)	0.066 4(3)
O(4)	0.025 1(1)	−0.053 0(3)	0.167 5(3)
O(5)	−0.139 7(1)	0.805 3(2)	0.631 8(3)
O(6)	0.146 5(1)	0.595 1(3)	1.048 8(3)
O(7)	0.159 8(1)	0.416 8(3)	0.934 6(3)
N(1)	−0.030 7(1)	0.261 1(2)	0.543 9(3)
N(2)	−0.058 8(1)	0.367 5(2)	0.574 5(3)
N(3)	−0.177 2(1)	0.210 3(2)	0.552 8(3)
N(4)	−0.036 0(1)	−0.063 2(3)	0.155 8(3)
N(5)	−0.120 5(1)	0.590 6(2)	0.593 5(3)
N(6)	0.127 2(1)	0.513 3(3)	0.955 1(3)
C(1)	−0.071 7(1)	0.171 8(3)	0.443 3(3)
C(2)	−0.140 0(1)	0.152 0(3)	0.446 2(3)
C(3)	−0.173 5(1)	0.062 4(3)	0.348 8(3)
C(4)	−0.140 2(2)	−0.005 0(3)	0.251 6(3)
C(5)	−0.072 0(2)	0.015 0(3)	0.254 3(3)
C(6)	−0.036 5(1)	0.100 8(3)	0.350 0(3)
C(7)	−0.182 9(2)	0.133 4(4)	0.685 3(4)
C(8)	−0.213 8(2)	0.318 3(3)	0.512 0(3)
C(9)	−0.258 6(2)	0.367 5(4)	0.618 2(4)
C(10)	−0.024 1(1)	0.454 8(3)	0.677 1(3)
C(11)	−0.061 1(1)	0.569 9(3)	0.691 0(3)
C(12)	−0.037 8(2)	0.658 9(3)	0.801 7(3)
C(13)	0.023 6(2)	0.640 3(3)	0.889 0(3)
C(14)	0.061 0(1)	0.532 2(3)	0.866 2(3)
C(15)	0.038 2(2)	0.438 1(3)	0.764 5(3)
C(16)	−0.153 8(2)	0.706 8(3)	0.563 8(4)
C(17)	−0.208 9(2)	0.700 9(4)	0.436 4(4)

Table 4. Compound (**12**): positional parameters and their estimated standard deviations.

Atom	x	y	z
Cl	0.625 6(2)	0.103 4(1)	0.771 4(1)
O(1)	0.032 0(8)	0.049 6(6)	0.629 4(5)
O(2)	0.257 7(9)	0.161 5(5)	0.660 1(5)
O(3)	0.751 2(6)	−0.312 4(4)	1.123 3(3)
O(4)	0.984 0(5)	−0.132 6(3)	1.066 3(3)
N(1)	0.182 3(6)	0.071 6(4)	0.676 1(3)
N(2)	0.492 1(6)	−0.247 2(4)	1.002 8(3)
N(3)	0.735 0(5)	−0.069 3(4)	0.943 3(3)
C(1)	0.466 3(7)	0.000 2(4)	0.808 4(4)
C(2)	0.270 2(7)	−0.010 9(4)	0.760 8(4)
C(3)	0.150 1(6)	−0.099 6(5)	0.789 2(4)
C(4)	0.223 0(6)	−0.178 7(4)	0.869 7(4)
C(5)	0.417 7(6)	−0.168 5(4)	0.921 3(3)
C(6)	0.686 0(7)	−0.243 2(5)	1.054 2(4)
C(7)	0.815 6(7)	−0.143 6(4)	1.021 0(4)
C(8)	0.540 4(6)	−0.078 6(4)	0.890 9(3)
C(9)	0.368 1(8)	−0.343 6(5)	1.033 2(4)

Table 5. Compound (**13**)·H_2O: positional parameters and their estimated standard deviations.

Atom	x	y	z
O(1)	−0.219 0(1)	0.351 3(4)	0.683 2(1)
O(2)	−0.104 1(1)	0.237 7(4)	0.735 3(1)
O(3)	0.088 8(1)	0.232 8(3)	0.345 9(1)
O(4)	0.182 2(1)	0.104 5(3)	0.469 4(1)
O(5)	0.119 5(1)	0.087 3(2)	0.599 0(1)
N(1)	−0.147 9(1)	0.296 3(3)	0.681 3(1)
N(2)	−0.020 9(1)	0.289 3(3)	0.408 9(1)
N(3)	0.076 9(1)	0.169 4(3)	0.536 2(1)
C(1)	−0.034 8(1)	0.233 5(3)	0.608 6(1)
C(2)	−0.114 6(1)	0.300 6(3)	0.610 4(1)
C(3)	−0.164 0(1)	0.368 5(3)	0.548 9(1)
C(4)	−0.132 8(1)	0.366 2(3)	0.481 7(1)
C(5)	−0.053 1(1)	0.297 5(3)	0.476 6(1)
C(6)	0.058 8(1)	0.232 8(3)	0.403 9(1)
C(7)	0.112 6(1)	0.163 4(3)	0.473 0(1)
C(8)	−0.003 9(1)	0.234 2(3)	0.541 2(1)
C(9)	−0.074 6(2)	0.334 2(4)	0.339 6(1)
O(W)	0.229 4(1)	0.333 7(3)	0.653 0(1)

192 (71), 163 (31), 152 (78), 151 (82), *etc.*; *X*-ray crystal structure, see Figure 4.

(*ii*) *Detection of formaldehyde.* In a second experiment, sodium ethoxide [from sodium, 0.34 g (15 mmol)] in ethanol (40 cm^3) was added at room temperature to a stirred solution of the ester (**7b**) (4.25 g, 15 mmol) in ethanol (110 cm^3) and dimethylformamide (50 cm^3), in a flask connected to a trap containing a solution of 2,4-dinitrophenylhydrazine in aqueous methanolic sulphuric acid. The reaction mixture was heated slowly to 40–45 °C, and kept at that temperature for 2 h; *ca.* 20 cm^3 of the mixture was then distilled into the trap, and the solution in the latter concentrated under reduced pressure until a small precipitate appeared. The mass spectrum of this ($M^{+\bullet}$, 210) corresponded to that of formaldehyde 2,4-dinitrophenylhydrazone.

(*iii*) *With potassium carbonate.* A solution of the ester (**7b**) (2.0 g, 7.1 mmol) and potassium carbonate (0.98 g, 7.1 mmol) in dimethylformamide (30 cm^3) and ethanol (50 cm^3) was stirred

Table 6. Molecular dimensions of compound (**8**).

(*a*) Bond distances (Å)

O(1)–N(1)	1.256(3)	N(6)–C(14)	1.463(4)
O(2)–C(8)	1.219(4)	C(1)–C(2)	1.382(4)
O(3)–N(4)	1.213(3)	C(1)–C(6)	1.382(4)
O(4)–N(4)	1.215(4)	C(2)–C(3)	1.384(4)
O(5)–C(16)	1.200(4)	C(3)–C(4)	1.366(4)
O(6)–N(6)	1.222(4)	C(4)–C(5)	1.372(4)
O(7)–N(6)	1.216(4)	C(5)–C(6)	1.368(4)
N(1)–N(2)	1.278(3)	C(8)–C(9)	1.493(5)
N(1)–C(1)	1.465(3)	C(10)–C(11)	1.411(4)
N(2)–C(10)	1.407(4)	C(10)–C(15)	1.388(4)
N(3)–C(2)	1.432(4)	C(11)–C(12)	1.393(4)
N(3)–C(7)	1.460(4)	C(12)–C(13)	1.377(4)
N(3)–C(8)	1.354(4)	C(13)–C(14)	1.370(5)
N(4)–C(5)	1.464(4)	C(14)–C(15)	1.373(4)
N(5)–C(11)	1.395(3)	C(16)–C(17)	1.484(5)
N(5)–C(16)	1.376(4)		

(*b*) Bond angles (°)

O(1)–N(1)–N(2)	127.4(2)	N(4)–C(5)–C(4)	118.4(3)
O(1)–N(1)–C(1)	115.8(2)	N(4)–C(5)–C(6)	119.3(3)
N(2)–N(1)–C(1)	116.7(2)	C(4)–C(5)–C(6)	122.2(3)
N(1)–N(2)–C(10)	120.0(2)	C(1)–C(6)–C(5)	118.0(3)
C(2)–N(3)–C(7)	116.1(2)	O(2)–C(8)–N(3)	121.0(3)
C(2)–N(3)–C(8)	117.9(2)	O(2)–C(8)–C(9)	122.3(3)
C(7)–N(3)–C(8)	124.8(3)	N(3)–C(8)–C(9)	116.7(3)
O(3)–N(4)–O(4)	123.5(3)	N(2)–C(10)–C(11)	112.3(2)
O(3)–N(4)–C(5)	118.4(3)	N(2)–C(10)–C(15)	128.3(3)
O(4)–N(4)–C(5)	118.1(3)	C(11)–C(10)–C(15)	119.4(3)
C(11)–N(5)–C(16)	127.0(2)	N(5)–C(11)–C(10)	118.8(2)
O(6)–N(6)–O(7)	123.1(3)	N(5)–C(11)–C(12)	121.9(3)
O(6)–N(6)–C(14)	117.9(3)	C(10)–C(11)–C(12)	119.3(3)
O(7)–N(6)–C(14)	119.1(3)	C(11)–C(12)–C(13)	120.5(3)
N(1)–C(1)–C(2)	123.1(3)	C(12)–C(13)–C(14)	119.0(3)
N(1)–C(1)–C(6)	115.4(2)	N(6)–C(14)–C(13)	119.5(3)
C(2)–C(1)–C(6)	121.3(3)	N(6)–C(14)–C(15)	117.9(3)
N(3)–C(2)–C(1)	123.8(2)	C(13)–C(14)–C(15)	122.5(3)
N(3)–C(2)–C(3)	117.6(2)	C(10)–C(15)–C(14)	119.0(3)
C(1)–C(2)–C(3)	118.3(3)	O(5)–C(16)–N(5)	124.1(3)
C(2)–C(3)–C(4)	121.2(3)	O(5)–C(16)–C(17)	122.2(3)
C(3)–C(4)–C(5)	118.7(3)	N(5)–C(16)–C(17)	113.7(3)

(*c*) Intra- and inter-molecular dimensions

Intramolecular hydrogen bond

N(5)H · · · N(2)	2.622(3)
HN(5) · · · N(2)	2.22
N(5)–H · · · N(2)	104

Intermolecular contacts

O(1)–O(3) (I)	3.281(3)
O(1)–O(4) (I)	3.158(3)
O(1)–O(5) (II)	3.189(3)
O(1)–N(4) (I)	2.862(3)
O(1)–N(5) (II)	3.232(3)
O(3)–O(4) (III)	3.083(4)
O(3)–O(7) (I)	3.430(4)
O(4)–O(4) (III)	3.262(3)
O(4)–N(1) (I)	3.379(3)
O(4)–N(4) (III)	3.211(4)

The roman numerals refer to the following equivalent positions:

(I) $-x, -y, 1-z$
(II) $-x, 1-y, 1-z$
(III) $-x, -y, -z$.

room temperature for 4 h, and the products isolated as in (*i*), above. The azoxybenzene (**9**) and the quinoxalinedione (**13**) were produced in 4 and 35% yield, respectively.

Table 7. Molecular dimensions for compound (**12**).

(*a*) Bond lengths (Å)

Cl–C(1)	1.706(5)
O(1)–N(1)	1.130(6)
O(2)–N(1)	1.145(8)
O(3)–C(6)	1.202(6)
O(4)–C(7)	1.211(5)
N(1)–C(2)	1.472(6)
N(2)–C(5)	1.394(6)
N(2)–C(6)	1.385(6)
N(2)–C(9)	1.457(7)
N(3)–C(7)	1.341(6)
N(3)–C(8)	1.397(5)
C(1)–C(2)	1.390(6)
C(1)–C(8)	1.404(6)
C(2)–C(3)	1.369(7)
C(3)–C(4)	1.385(6)
C(4)–C(5)	1.395(6)
C(5)–C(8)	1.401(6)
C(6)–C(7)	1.521(7)

(*b*) Bond angles (°)

O(1)–N(1)–O(2)	119.0(6)
O(1)–N(1)–C(2)	119.4(5)
O(2)–N(1)–C(2)	121.4(4)
C(5)–N(2)–C(6)	122.7(4)
C(5)–N(2)–C(9)	120.1(4)
C(6)–N(2)–C(9)	117.1(4)
C(7)–N(3)–C(8)	123.9(4)
Cl–C(1)–C(2)	123.9(4)
Cl–C(1)–C(8)	117.4(3)
C(2)–C(1)–C(8)	118.7(4)
N(1)–C(2)–C(1)	121.2(4)
N(1)–C(2)–C(3)	116.8(4)
C(1)–C(2)–C(3)	122.0(4)
C(2)–C(3)–C(4)	119.6(4)
C(3)–C(4)–C(5)	120.3(4)
N(2)–C(5)–C(4)	120.7(4)
N(2)–C(5)–C(8)	119.5(4)
C(4)–C(5)–C(8)	119.8(4)
O(3)–C(6)–N(2)	122.8(5)
O(3)–C(6)–C(7)	120.3(4)
N(2)–C(6)–C(7)	116.9(4)
O(4)–C(7)–N(3)	122.7(5)
O(4)–C(7)–C(6)	119.6(4)
N(3)–C(7)–C(6)	117.7(4)
N(3)–C(8)–C(1)	121.1(4)
N(3)–C(8)–C(5)	119.3(4)
C(1)–C(8)–C(5)	119.6(4)

(*c*) Hydrogen bond dimensions (Å and °)

N(3) · · · O(4) (I)	2.949(5)
H(N3) · · · O(4) (I)	2.04
N(3)–H · · · O(4) (I)	160

The roman numeral refers to the equivalent position $2-x, -y, 2-z$.

(*iv*) *With triethylamine.* The ester (**7b**) (3.0 g), triethylamine (1.07 g, 1 mol equiv.) and ethanol (50 cm^3) were heated together, under reflux, for 4 h, and the products separated as in (*i*). The acetone-insoluble product was identified as the symmetrically substituted azoxybenzene derivative (**10**) (7%); a small amount (1%) of the quinoxalinedione (**13**) was also obtained.

Repetition of the experiment with 2 mol equiv. of triethylamine gave (**10**) (16%) as the only isolated product.

(*v*) *With triethylamine in the presence of* o-*phenylenediamine.* A solution of the ester (1.0 g, 3.5 mmol) and *o*-phenylenediamine (0.38 g, 3.5 mmol) in ethanol (25 cm^3) was heated under reflux for 1 h; no reaction was observed (t.l.c.). Triethylamine (0.71 g, 2 mol equiv.) was then added, and heating continued for 4.5 h. The mixture was cooled and the red–brown precipitate filtered off, washed with ethanol (200 cm^3), and recrystallised from dimethylformamide, to give the azoxy compound (**10**) (0.29 g, 48%).

The reaction mother liquor was evaporated to dryness under reduced pressure, and the residue was extracted with a mixture of water and dichloromethane. The product, which was insoluble in both layers, on recrystallisation from ethanol (with charcoal), gave quinoxalin-2-one (**16**), m.p. 258–260 °C, (lit.,[15] 262–264 °C): $\nu_{max.}$ 1 695 cm^{-1} (C=O); δ_H 7.19–7.86 (4 H, m, 5-, 6-, 7-, and 8-H), 8.19 (1 H, s, 3-H), and 13.53 (1 H, br, NH); *m/z* 146 ($M^{+\bullet}$), 118, 91.

The dichloromethane layer, when dried and evaporated, gave a tarry residue (0.69 g), t.l.c. of which indicated a mixture of at least 8 compounds.

Table 8. Molecular dimensions for compound (**13**)·H_2O.

(*a*) Bond distances/Å

O(1)–N(1)	1.218(3)
O(2)–N(1)	1.207(3)
O(3)–C(6)	1.220(3)
O(4)–C(7)	1.210(3)
O(5)–N(3)	1.386(2)
N(1)–C(2)	1.463(3)
N(2)–C(5)	1.401(3)
N(2)–C(6)	1.363(3)
N(2)–C(9)	1.469(3)
N(3)–C(7)	1.354(3)
N(3)–C(8)	1.398(3)
C(1)–C(2)	1.378(3)
C(1)–C(8)	1.385(3)
C(2)–C(3)	1.376(3)
C(3)–C(4)	1.384(3)
C(4)–C(5)	1.391(3)
C(5)–C(8)	1.403(3)
C(6)–C(7)	1.514(3)

(*b*) Bond angles/°

O(1)–N(1)–O(2)	122.7(2)
O(1)–N(1)–C(2)	118.4(2)
O(2)–N(1)–C(2)	118.9(2)
C(5)–N(2)–C(6)	122.3(2)
C(5)–N(2)–C(9)	120.2(2)
C(6)–N(2)–C(9)	117.4(2)
O(5)–N(3)–C(7)	117.9(2)
O(5)–N(3)–C(8)	116.8(2)
C(7)–N(3)–C(8)	124.9(2)
C(2)–C(1)–C(8)	117.9(2)
N(1)–C(2)–C(1)	117.9(2)
N(1)–C(2)–C(3)	119.0(2)
C(1)–C(2)–C(3)	123.0(2)
C(2)–C(3)–C(4)	118.4(2)
C(3)–C(4)–C(5)	120.8(2)
N(2)–C(5)–C(4)	121.8(2)
N(2)–C(5)–C(8)	119.3(2)
C(4)–C(5)–C(8)	118.8(2)
O(3)–C(6)–N(2)	123.0(2)
O(3)–C(6)–C(7)	118.1(2)
N(2)–C(6)–C(7)	118.9(2)
O(4)–C(7)–N(3)	124.0(2)
O(4)–C(7)–C(6)	120.2(2)
N(3)–C(7)–C(6)	115.7(2)
N(3)–C(8)–C(1)	120.4(2)
N(3)–C(8)–C(5)	118.7(2)
C(1)–C(8)–C(5)	120.9(2)

(*c*) Hydrogen bond dimensions (Å and °)

O(W)···O(1)*	3.013(2)
O(W)···O(2)*	3.129(3)
O(W)···O(3)#	2.968(2)
O(W)···O(4)#	2.838(2)
O(W)···O(5)	2.602(2)
O(W)---HW(1)	0.843
O(W)---HW(2)	0.794
O(W)···HO(5)	1.726
HW(1)···O(1)*	2.172
HW(2)···O(3)#	2.285
HW(2)···O(4)#	2.176

HW(1)---O(W)---HW(2)	123.2
HW(1)---O(W)···HO(5)	108.4
HW(2)---O(W)···HO(5)	111.5
O(W)---HW(1)···O(1)*	174.6
O(W)---HW(2)···O(3)#	144.5
O(W)---HW(2)···O(4)#	141.1
O(3)#···HW(2)···O(4)#	74.4
O(5)---HO(5)···OW	169.9

The * and # refer to equivalent positions: * $-x, y, 1.5 - z$; # $0.5 - x, 0.5 - y, 1 - z$.

2-*Acetamido*-2′-(N-*methylacetamido*)-5,5′-*dinitro*-ONN-*azoxybenzene* (**8**).—The azoxy compound (**9**) (0.25 g, 0.75 mmol) was stirred at room temperature in acetic anhydride (10 cm^3) containing concentrated sulphuric acid (2 drops). After 20 min, the yellow solution was added with stirring to ice–water (60 cm^3) and the *diamide* (**8**) filtered off. It had m.p. 190–194 °C (from ethanol) (Found: C, 49.2; H, 3.9; N, 20.3. $C_{17}H_{16}N_6O_7$ requires C, 49.0; H, 3.9; N, 20.2%); $\nu_{max.}$ 3 300(NH), 1 710 (CO), 1 555, and 1 335 cm^{-1} (NO_2); ^1H n.m.r. spectrum, see Table 1; *X*-ray crystal structure, see Figure 1.

Reaction of 1-*Hydroxy*-4-*methyl*-7-*nitroquinoxaline*-2,3-*dione* (**13**) *with Thionyl Chloride.*—Compound (**13**) (0.8 g) and thionyl chloride (25 cm^3) were heated together, under reflux, for 3 h. The excess of thionyl chloride was distilled off and the residue recrystallised from dimethylformamide–ethanol to give 5-*chloro*-1-*methyl*-6-*nitroquinoxaline*-2,3-*dione* (**12**), m.p. 278–283 °C (Found: C, 43.0; H, 2.3; N, 16.6. $C_9H_6ClN_3O_4$ requires C, 42.3; H, 2.4; N, 16.4%); $\nu_{max.}$ 1 675br (CO), 1 520 and 1 330 cm^{-1} (NO_2); δ_H 3.58 (3 H, s, CH_3), 7.55 (1 H, d, 8-H), 7.95 (1 H, d, 7-H): $J_{7,8}$ 9 Hz. Although the compound was slightly impure (contaminated by traces of starting material), *X*-ray crystallography was carried out successfully (Figure 3) on a single crystal.

1-*Hydroxy*-4-*methylquinoxaline*-2,3-*dione* (**21**).—(*i*) The literature method[5] was adapted as follows: *N*-cyanoacetyl-*N*-methyl-*o*-nitroaniline (1.1 g, 5 mmol) and aqueous sodium hydroxide (1 mol dm^{-3}; 10 cm^3) were heated together under reflux for 30 min, and the mixture then cooled, acidified (HCl) and extracted with chloroform. The extract was dried (Na_2SO_4) and evaporated to give the product (**21**) (0.51 g, 53%), m.p. 246 °C (decomp.) (from ethanol; lit.,[5] 253 °C, lit.,[6] 259–260 °C).

(*ii*) Sodium ethoxide (from sodium, 0.23 g) in ethanol (25 cm^3) was added to a solution of *N*-cyanoacetyl-*N*-methyl-*o*-nitroaniline (1.1 g) in ethanol (25 cm^3), and the mixture heated under reflux for 30 min, then evaporated to dryness. The residue was partitioned between water and dichloromethane. Careful acidification (HCl) of the aqueous layer, with stirring and cooling in ice, gave the quinoxaline (**21**), which was recrystallised from ethanol (with charcoal) (0.64 g, 69%); the m.p. was only 230 °C (decomp.), but the product was spectroscopically identical with that in (*i*).

Reaction of 1-*Hydroxy*-4-*methylquinoxaline*-2,3-*dione with Thionyl Chloride.*—The quinoxaline (**21**) (0.5 g) and thionyl chloride (15 cm^3) were heated together under reflux for 2.5 h. The excess of thionyl chloride was distilled off and the residue triturated with a mixture of ethanol and diethyl ether.

Recrystallisation of the resulting solid from dimethylformamide gave 3,7-*dichloro*-1-*methylquinoxalin*-2-*one* (**22**) (0.20 g, 34%), m.p. 248–249 °C (Found: C, 47.2; H, 2.6; N, 12.2. $C_9H_6Cl_2N_2O$ requires C, 47.2; H, 2.6; N, 12.2%); $\nu_{max.}$ 1 655 cm^{-1} (CO); δ_H 3.66 (3 H, s, CH_3), 7.46 (1 H, dd, 6-H), 7.74 (1 H, d, 8-H), 7.81 (1 H, d, 5-H); $J_{5,6}$ 8.5 Hz, $J_{6,8}$ 2.0 Hz.

X-*Ray Crystallography*.—Crystals of (**8**), (**12**), and (**13**)·H_2O suitable for *X*-ray diffraction experiments were grown from ethanol, dimethylformamide–ethanol, and methanol respectively. For each compound, cell data were determined on a CAD-4 diffractometer from the setting angle of 25 reflections with θ in the range 10–15° using Mo-K_α radiation.

Crystal Data.—*Compound* (**8**): $C_{17}H_{16}N_6O_7$, M_r = 416.4. Monoclinic, a = 19.949(4), b = 10.289(4), c = 9.101(2) Å, β = 97.98(2)°; U = 1 850 Å^3, Z = 4, D_c = 1.49 g cm^{-3}, $F(000)$ = 864, μ(Mo-K_α) = 1.1 cm^{-1}. Space group $P2_1/n$, uniquely from systematic absences.

Compound (**13**): $C_9H_6ClN_3O_4$, M_r = 255.6. Monoclinic, a = 6.922(1), b = 10.857(3), c = 13.192(2) Å, β = 100.87(1)°; U = 974 Å^3, Z = 4, D_c = 1.74 cm^{-3}, $F(000)$ = 520, μ(Mo-K_α) = 4.0 cm^{-1}. Space group $P2_1/c$, uniquely from systematic absences.

Compound (**13**·H_2O: $C_9H_7N_3O_5$·H_2O, M_r = 255.2. Monoclinic, a = 16.130(3), b = 7.173(1), c = 18.215(3) Å, β = 97.67(2)°; U = 2 088 Å^3, Z = 8, $F(000)$ = 1 056, μ(Mo-K_α) = 1.3 cm^{-1}. Space group $C2/c$ or Cc from systematic absences: $C2/c$ chosen and confirmed by the analysis. The crystals rapidly lose solvent when left to stand in air; for the analysis, a freshly prepared crystal was removed from the mother liquor and coated with a thin layer of cement.

Data Collection and Processing.—Data were collected with a CAD-4 diffractometer, using the ω/2θ scan method and graphite-monochromatised Mo radiation. Details for the three compounds are given in Table 2. The structures were solved with the aid of MULTAN, and refined by full-matrix least-squares calculations with all non-hydrogen atoms allowed anisotropic motion. All hydrogen atoms were clearly visible in difference maps calculated at intermediate stages in the refinements, and all were included (but not refined) in the final rounds of calculations. For all three structures, the N–H and C–H hydrogens were positioned geometrically 0.95 Å from the atom to which they were bonded. For (**13**)·H_2O, the co-ordinates of hydrogens bonded to oxygen were taken from the difference maps. For (**8**), one of the methyl groups (C-17 in Figure 1) had its hydrogens disordered equally over two sites.

The weights used in the refinement were based on counting statistics $w = 1/[\sigma^2(F) + p(F_o^2)]$ and scattering factor data were from International Tables for *X*-ray Crystallography.[20] All calculations were performed on a PDP11/73 system using SDP-Plus.[21]

Final fractional co-ordinates for (**8**), (**12**), and (**13**)·H_2O are in Tables 3, 4, and 5, and details of dimensions are in Tables 6, 7, and 8. Tables of calculated hydrogen co-ordinates, anisotropic thermal parameters, mean-plane calculations, and structure-factor listings for all three compounds have been deposited at the Cambridge Crystallographic Data Centre.* Views of the three compounds are in Figures 1, 3, and 4.

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